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FINAL REPORT: CONTRACT N00019-69-C-0133

CODE - AIR-52032A

SEPTEMBER 1969

# DEVELOPMENT OF A PROCESS FOR PRODUCING TRANSPARENT SPINEL BODIES

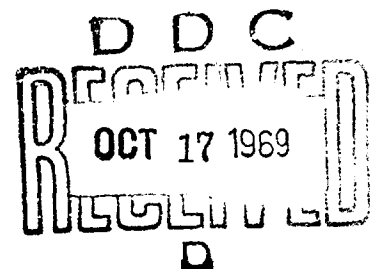
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## SUMMARY

This final report covers the period from 15 September 1968 to 15 September 1969. The work was performed under Contract No. N00019-69-C-0133, Code AIR-52032A with Mr. C. Bersch of Naval Air Systems Command serving as Program Monitor.

A few transparent spinel samples have been made. Present studies involve the improvement of reproducibility and the characterization of the process and the material it produces. The results recorded thus far in the study are enumerated below:

- 1) A process for producing high purity, fine grained, dense spinel powders has been demonstrated.
- 2) A sintering furnace has been built which is cam controlled and is capable of maintaining temperatures of 1950°C for long times in hydrogen atmosphere. Other atmospheres can be introduced by using a molybdenum retort through which various gases, such as steam and wet hydrogen, can be piped.
- 3) A few transparent specimens of both Composition A and Composition B have been made.
- 4) Thus far, additions of  $\text{SiO}_2$  and  $\text{LiO}_2$  are necessary to produce the transparent spinel materials.
- 5) Densities greater than 99% of theoretical are readily reached by most of the materials after sintering for one hour or longer at 1900°C in hydrogen. These specimens appear vitreous and are translucent or nearly transparent in thin sections (about 0.060 in. thick). Transparent specimens have been produced by sequential firing schedules which couple increasing temperatures with decreasing times at temperature. A typical 48 hour firing schedule would be 20 hours at 1600°C, 8 hours at 1700°C, 8 hours at 1800°C, and 8 hours at 1900°C in hydrogen atmosphere.
- 6) Steam appeared to be a promising atmosphere for sintering spinels. Steam, rather than hydrogen, would have decided advantages in terms of cost and safety. However, firing schedules which produce transparent spinel in hydrogen atmosphere have not been duplicated in steam as yet.

## I. INTRODUCTION

The need for hard, strong, high modulus transparent materials has been established, especially for windows acting as protection against armor piercing projectiles. Such a class of materials is available and includes systems containing glasses (noncrystalline) and ceramics (crystalline). The glasses have proved insufficient because of the thickness necessary to defeat present projectiles. The ceramic materials (although highly effective) are at present expensive in single-crystal form and are severely size and shape limited. The development of a process that can produce ceramic materials without these limitations is the goal of the present study. The ceramic chosen for investigation was Magnesium-Aluminum Spinel ( $\text{Mg Al}_2\text{O}_4$ ), because of its acceptable ballistic properties and its cubic, isotropic, crystal structure, which assured acceptable optical properties. Recent work has been very encouraging in that small, thin specimens of spinel composition have been made that have a high degree of transparency and are at least 99.9% dense.

The experimental approach used was that of controlling material and processing parameters such that the probable attainment of transparency was maximized. The approach included:

- 1) The production of fine-particle ( $\sim 0.2\mu$ ) active-sintering spinel powders of theoretical density by combining mixtures of aluminum and magnesium salts.
- 2) The utilization of commercially available high-purity, fine-particle alumina and magnesia.
- 3) Powder compositions that bracket the spinel phase field.
- 4) The addition of  $\text{SiO}_2$  and  $\text{Li}_2\text{O}$  as sintering aids to control grain boundary migration rates.
- 5) Powder processing to maximize starting density.
- 6) Sintering times, temperatures, and atmosphere control to maximize final density.

## II. BACKGROUND

The requirement of transparency is a stringent one and densities greater than 99.9% of theoretical are necessary before acceptable clarity can be realized. For example, the measurement of densities requires extreme precision, but the data would only indicate that the material was approaching clarity. The most critical test is simple, look through it.

It was decided to follow density change and shrinkage with sufficient precision to access pertinent sintering parameters but to concentrate the total effort on reaching transparency rather than accumulating data for its own sake.

The ability to sinter oxide materials to full density requires that certain conditions be met and maintained throughout processing. These requirements are discussed below in detail.

### A. Starting Powder

The starting powders must be of high purity (to avoid second phase, discoloration, etc.), capable of active sintering (less than  $1\mu$  diameter), fully dense (contains no porosity) and of uniform grain-size to provide an essentially uniform porosity field (as a means of controlling porosity agglomeration and discontinuous grain growth).

### B. Powder Processing

Powder processing must be controlled so that powder purity is maintained. This usually involves good housekeeping practices and great care as to choice of liquid media, mixing apparatus, milling devices, etc. Metal contamination usually leads to "measle" formation (non-uniform porosity) and discoloration (both as an oxide discoloration, such as pink due to chromium or blackening due to reduced metal dispersions). Non-metallic contamination is usually seen as opaque second phases or glassy films. All processing was performed using plastic containers and plastic coated stirrers. All other processing equipment utilized aluminum parts to limit metal contamination.

### C. Sample Preparation

As a rule, active sintering powders are bulky. Since it has been shown (1) that green densities greater than 35% and preferably about 50% are necessary to achieve full density after sintering, steps to increase the green density are usually employed. This could involve spray drying, the addition of lubricants, precompaction and granulation.

All of the powder compacting techniques have produced high density material in the past (1), including slip-casting die pressing and hydrostatic pressing as long as green density requirements are



met. Steel die pressing at 20,000 psi pressure was used throughout. Calcined powders were prepressed, cleaned, granulated, and final pressed as small disks (3/4 in. dia. by 1/8 in. thick). During these operations, processed powders were handled carefully and stored again to minimize contamination.

#### D. Sintering

The requirements of theoretical density demands that all porosity initially present in a powder compact be removed. It has been established (2) that porosity can be removed by sintering (in a reasonable amount of time) as long as the porosity remains on grain boundaries which, in turn, act as sinks for rapid vacancy transport. If porosity becomes entrapped within grains (see Figure 1) then bulk diffusion must be relied upon to remove vacancies. This diffusion process is so slow that for all practical purposes sintering ceases, negating any chance that theoretical density can be reached.



*Figure 1. Example of Discontinuous Grain Growth Leading to Pore Entrapment*

Techniques are available which can control porosity orientation so that it remains along grain boundaries. Porosity can be utilized as a second phase which inhibits grain-boundary migration (3). However, if pore size diminishes and judicious control of time and temperature is not maintained, the boundaries can break-away, entrapping porosity which stops the sintering process. Other second-phase particles might also be used, such as CaO in ThO<sub>2</sub> (4) (Thoralex<sup>®</sup>).

A second mechanism, which has proved effective during the development of Lucalox<sup>®</sup> and Yttralox<sup>®</sup>, is the grain-boundary migration restraint induced by minor impurities. This occurs through solute segregation at grain boundaries during final-stage sintering (5) (6).

<sup>®</sup> Registered trade marks for dense ceramic products of the General Electric Co.

The role of atmosphere is also important. During powder processing, entrapment of atmospheric gases within the porous structure cannot be avoided. Also, during final firing, gas entrapment can occur within pores. It is, therefore, essential that either the pores contain no gases during firing (i.e., vacuum sintering) or contain only those gases which can diffuse easily through the atomic structure of the material. For most oxide materials, including spinel, hydrogen has proved to be an ideal atmosphere. Spinel is somewhat unique, however, in that the MgO constituent is fugitive (volatile) in the hydrogen atmosphere at the sintering temperatures necessary to achieve transparency. Thus extra precautions must be taken to insure that adequate MgO vapor pressure is available to minimize MgO loss within the ware. If this is not done, pore formation by volatilization becomes dominant and no transparent material can be made.

Atmosphere control, sequential firing, and the addition of sintering aids and/or second phases were all found to be necessary. The control of these parameters and the possibility of ultimately developing transparent spinel comprise the remainder of this report.

### III. Experimental Procedures

#### A. Powder Processing

This study was directed entirely toward transparency, without consideration of other mechanical or physical properties, and has produced some encouraging results.

The techniques used to produce intimately-mixed, fine-grained, fully-dense spinel powders were both a "salt" approach and the use of commercially available oxides. The salt approach involved dissolving appropriate amounts of a mixture of high-purity magnesium sulfate ( $\text{Mg SO}_4 \cdot 7\text{H}_2\text{O}$ ) and ammonia-aluminum alum ( $\text{Al}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ ) in distilled water. The solution was boiled to remove excess water and the resulting salt mixtures were calcined at  $1250^\circ\text{C}$  to convert the salts to spinel-oxide mixtures. A flow diagram of the technique is shown in Figure 2. This process produced the thin clear spinel plates shown in Figure 3.

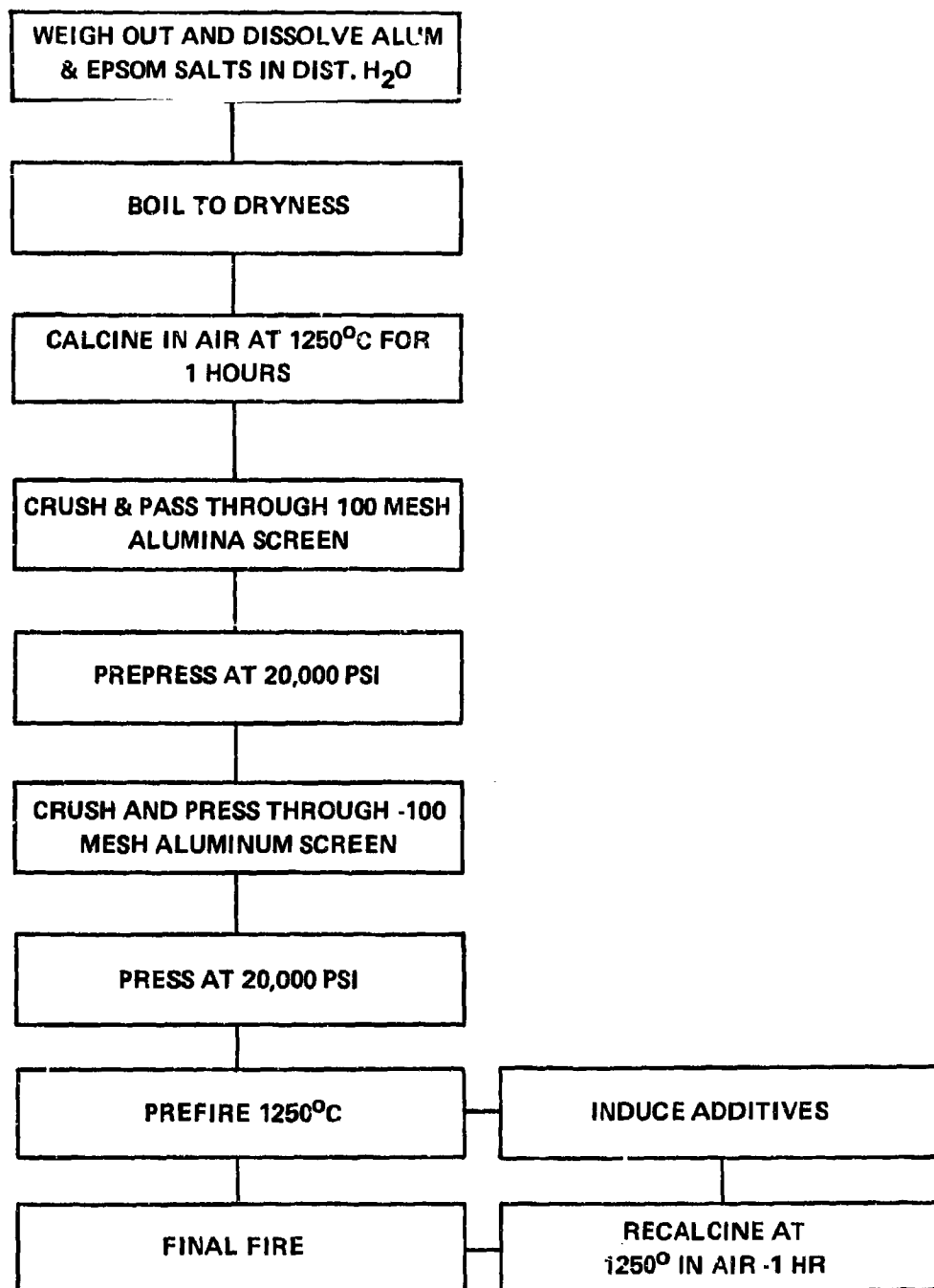
Inherent in the "salt" process is the concentrating of impurities because of the large decrease in volume associated with calcination of the alum, which affected the color of the sintered material. Also, the processing of large volumes of liquid is necessary to produce relatively small amounts of oxide materials. The processing of many different compositions then becomes rather arduous, especially when additives were found to be beneficial. Consequently, when a transparent material was finally produced, commercially available oxide powders were successfully substituted. The powders utilized were Linde "A" alumina and freshly calcined Baker USP grade  $\text{MgO}$ , intimately mixed by using an aluminum-bladed Warning Blendor<sup>®</sup> with pure grain alcohol as the liquid media. The mixed slurry was dried, calcined at  $1250^\circ\text{C}$ , and crushed. The flow diagram for this approach is shown in Figure 4.

The following compositions were studied extensively:

- 1) Composition A — 50-50  $\text{MgO}:\text{Al}_2\text{O}_3$  Mole %
- 2) Composition B — 62-38  $\text{MgO}:\text{Al}_2\text{O}_3$  Mole %
- 3) Composition C — 25-75  $\text{MgO}:\text{Al}_2\text{O}_3$  Mole %.

The materials described above represent compositions which straddle the spinel phase at  $1900^\circ\text{C}$ . Their positions in the magnesia-alumina phase diagram are indicated schematically in Figure 5. The resulting active-sintering powders were of high purity and fully dense.

Figures 2 and 4 contain information which follows the processing steps to the final firing stage. Each step was studied by observing the materials' response to sintering as a function of both shrinking parameters and final density. Each step was found to add to the final density of the



*Figure 2. Flow Diagram of Salt Mixture Powder Processing*



*Figure 3. Spinel Plates Formed After Calcining Mixture A for 1 Hour at 1100°C in Air*

material and thus was deemed necessary to reach the final goal of transparency. Repeated efforts to simplify the processing led to less dense material. Thus all subsequent sintering studies were performed using these processing steps. One further processing innovation seems worthy of mention. As implied earlier, initial results were obtained using starting powders made by the "salt" process. However, additives were found necessary to achieve transparency and rather than processing a large volume of materials, the expedient technique of inoculation was used. This consisted of making carefully controlled water solutions of both potassium silicate (for  $\text{SiO}_2$  additives) and lithium chloride (for  $\text{Li}_2\text{O}$  additives) and inoculating pressed and prefired samples so that the samples would contain approximately 2% by weight of additives after recalcining. This technique proved to be an expeditious tool and will be used in future work to survey other additives of similar atomic position or chemical behavior. Additives to powders processed more conventionally were made by introducing Silica and lithium carbonate as powders during mixing.

#### **B. Calcination and Compaction**

Special precautions were necessary during calcining of the mixed salt material since 90% of their weight is composed of volatiles including water and ammonium sulfate. A hood was constructed over a conventional Harper Glow-bar fired furnace and the resulting fumes vented to the outside. After calcination, a crumbly, frothy cake resulted which was crushed by mortar and pestle.

Mixed oxide powders were easily crushed and screened. Precompaction and final pressing was done in conventional steel dies lubricated with trichlorethylene paraffin mixture at a pressing pressure of

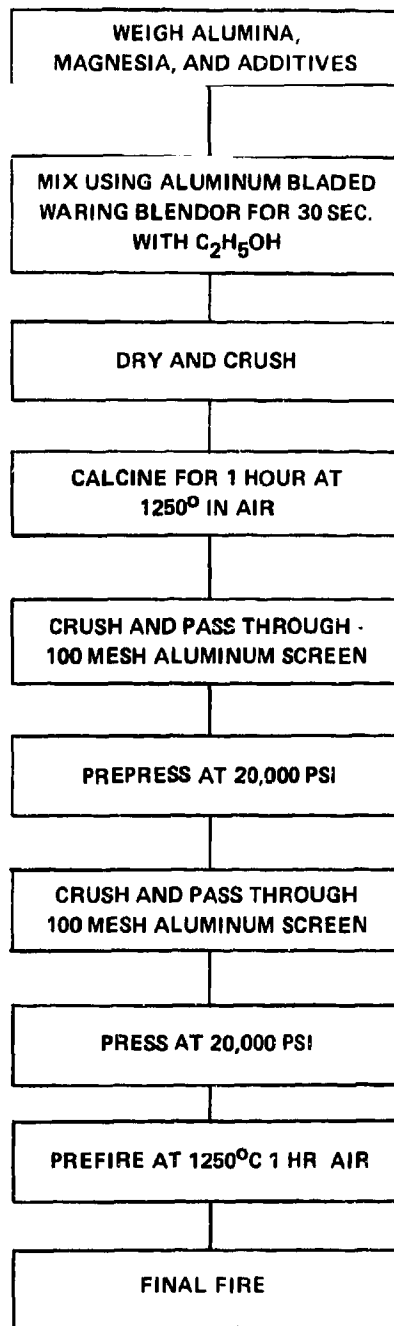


Figure 4. Flow Diagram of Linde A-Baker Magnesia Powder Processing

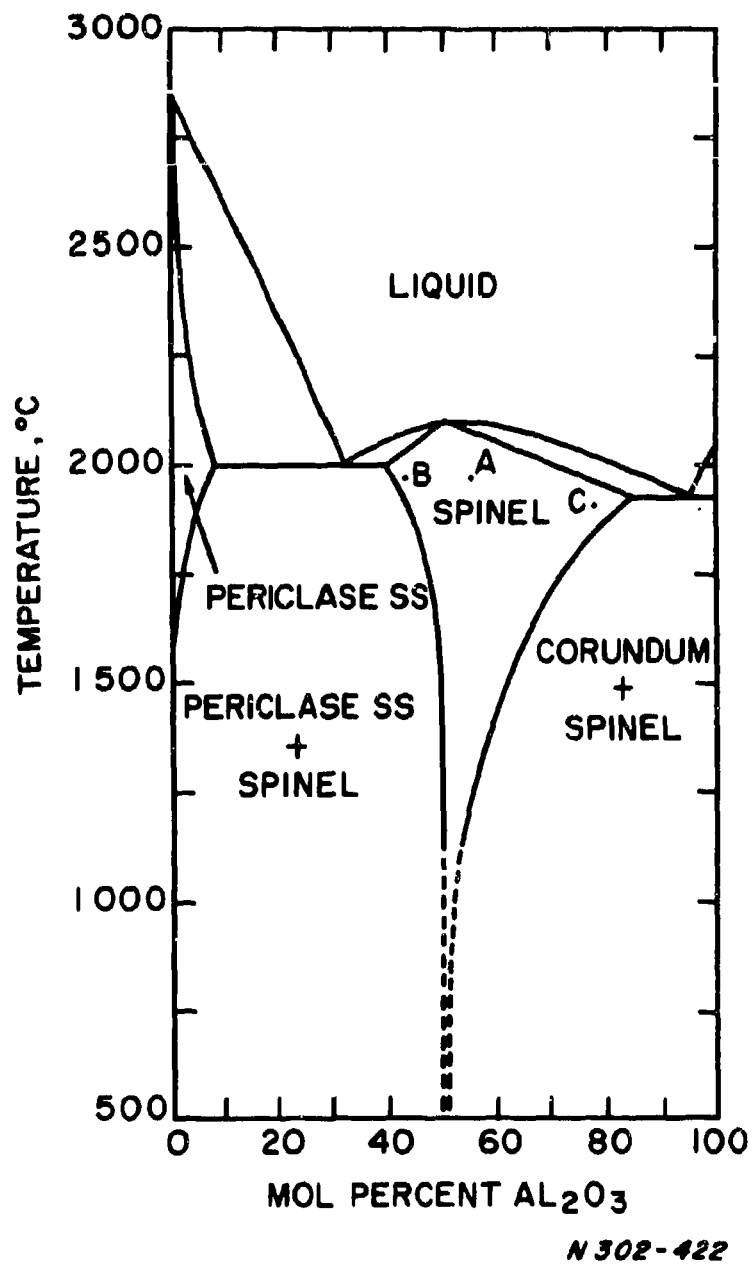


Figure 5. Phase Diagram for the  $\text{MgO}-\text{Al}_2\text{O}_3$  System

20,000 psi. Precompaction always added to the final density of the spinel material after final firing and thus became a routine procedure. Most of the metal pickup from the pressing die walls, which was always present on a pressed pellet outside surface, was removed by scraping before firing to reduce contamination.

### C. Sintering

Prefiring (or biscuit firing) of the final pressed samples served two purposes. First, prefired material always achieved a higher density than material which had not been prefired. Secondly, prefired samples were not as fragile and were, therefore, easier to weigh, measure, etc. Adhering to the philosophy of maximizing density, prefiring also became a routine procedure. Prefiring was carried out in a Century furnace held at 1250°C. Samples placed in alumina boats were slowly pushed into the hot zone and after one hour were slowly withdrawn.

Sintering was carried out using three different atmospheres: air, steam, and hydrogen. Air and steam firings were performed using a 60-40 pt-rd wound furnace with a maximum operating temperature of 1820°C. For air atmosphere, alumina boats containing samples were placed in the furnace and the current regulated until 1800°C was attained. Steam firings at the same temperature were performed using apparatus described in Figure 6. The temperature limitation imposed by the pt-rd resistance furnace precluded any chance that these studies would produce transparent material, and indeed no acceptable material was made.

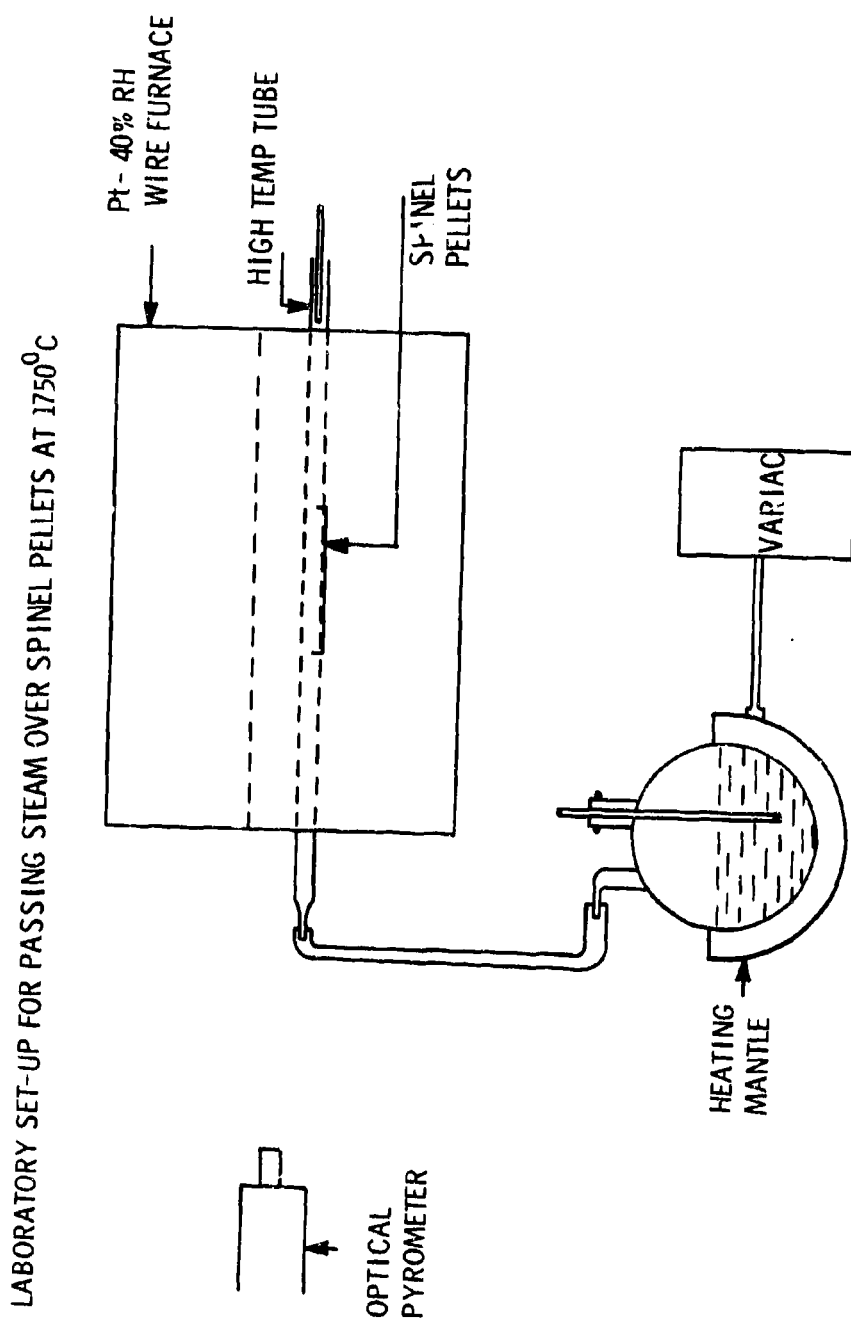
A hydrogen furnace previously designed by the GE Research Laboratory, using special high-purity alumina refractories and molybdenum windings capable of operating to 1950°C for extended periods, was used for hydrogen atmosphere sintering studies. Equipped with a West cam controlled recorder, this furnace could be controlled to operate at any time-temperature combination deemed necessary to the limit of the equipment. The versatility of this combination has not yet been surpassed.

Because MgO is fugitive at the sintering temperatures necessary to promote full density and therefore transparency, special procedures were followed to minimize MgO vapor loss. During air and steam firings, specimens were buried in powder of the same compositions in open boats. During hydrogen firing, the set-up shown schematically in Figure 7 was used. The cover reduced the tendency of the hydrogen stream to sweep vapor away while the platform raised the spinel powder above the specimens so that reaction of the specimens with the powder together with any crusting was avoided.

### D. Qualitative Density Measurements and Metallography

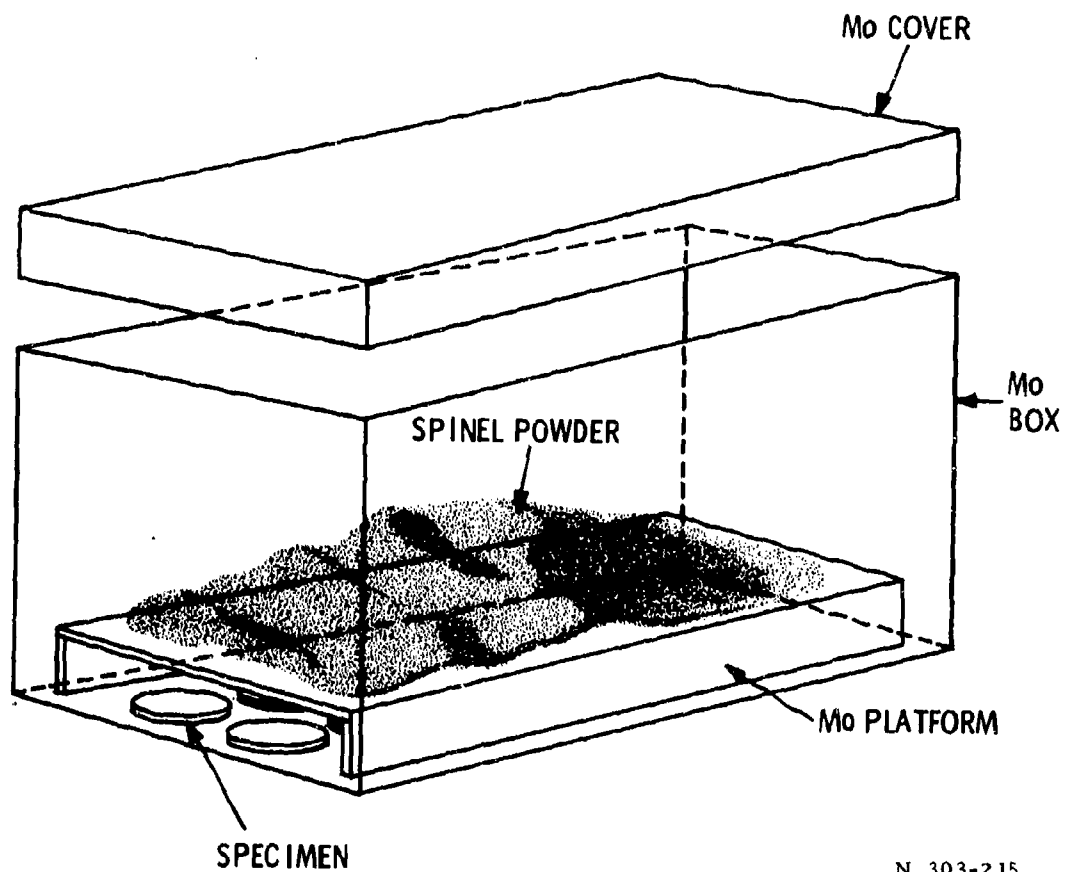
Linear shrinkage and density measurements were followed as a means of indicating to what degree each processing parameter studied was affecting final density. Micrometer measurements were made





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Figure 6. Schematic Diagram of Steam-Firing Apparatus



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*Figure 7. Schematic Representation of Hydrogen Firing Boat and Experimental Setup  
(About Actual Size)*

before and after each firing. Densities were determined by calculations from physical dimensions and by Archimedes principle. It is to be noted that densities greater than 99% of theoretical were readily achieved by most of the compositions studied. Transparency was the final criterion in determining which processing parameters and compositions were most capable of producing acceptable material.

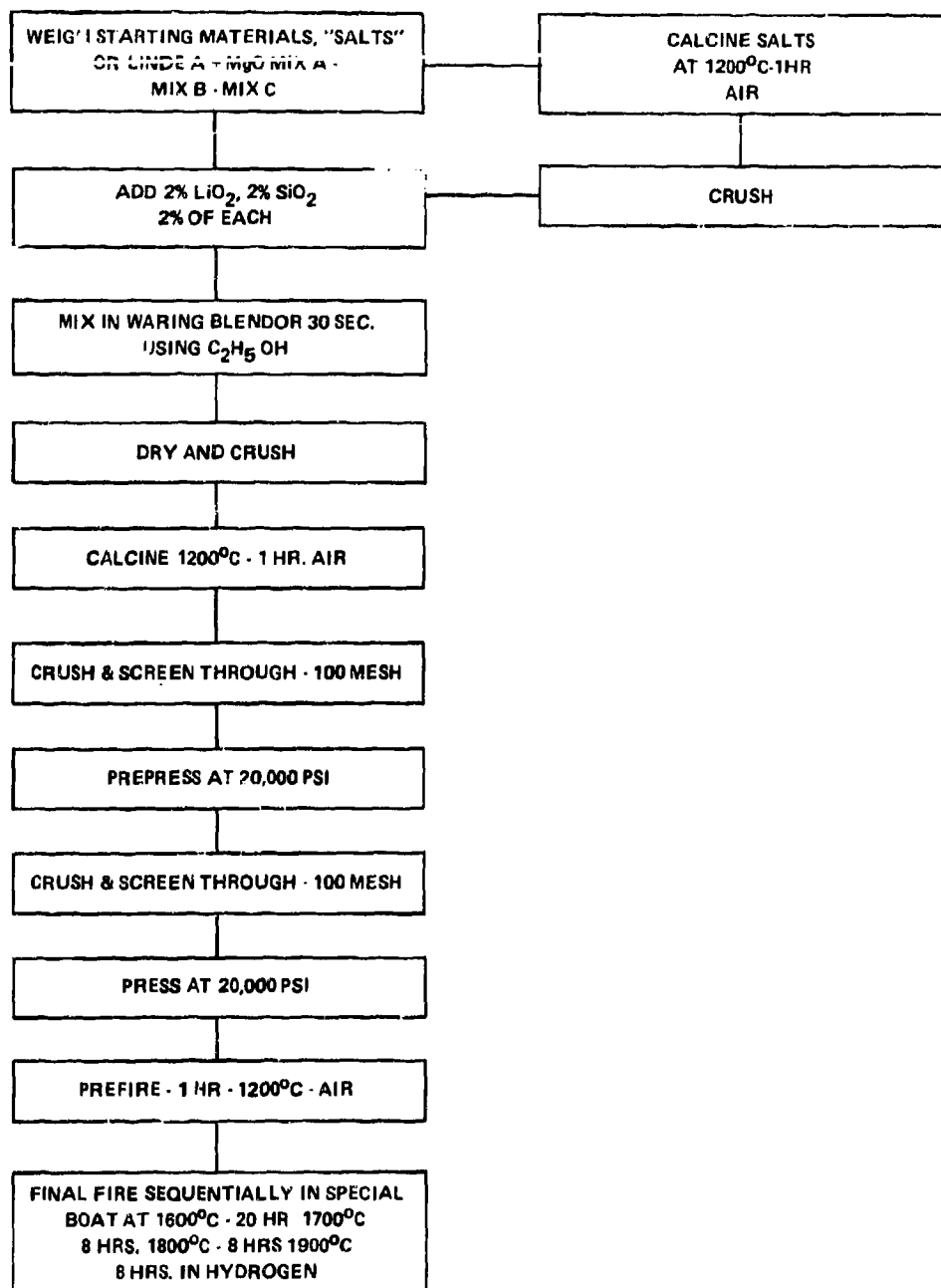
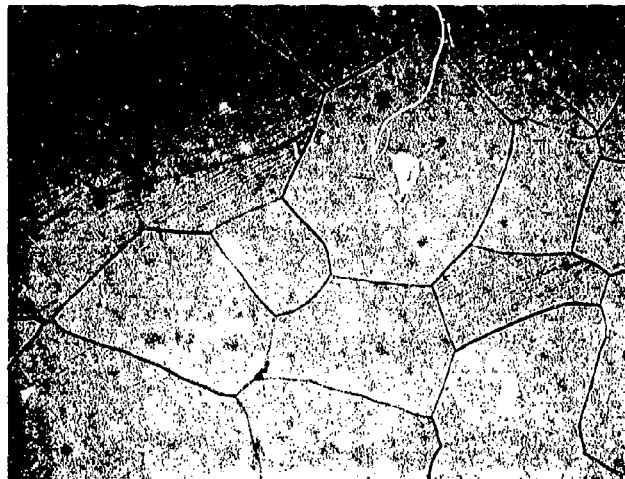


Figure 8. Processing Flow Chart for Producing Transparent Spinel

#### IV. RESULTS AND DISCUSSION

Transparent spinel has been produced by powder processing, using compositions A and B containing silica additives, lithia additives, and combinations of silica and lithia. No transparent material could be made with composition C; although dense, translucent material resulted. Thus far, disks 5/8 in. in diameter and 1/16 in. thick have been made. Figure 8 is a flow diagram of the process as developed. It is noted that present technology is of a preliminary and cursory nature. Much work remains to thoroughly characterize both the processing parameters and the material produced. Table I contains a summary of the compositions studied. Not all firings are recorded but the data presented is a chronological representation of critical experiments which led to the attainment of the transparency.

Figure 9 is a typical microstructure of transparent spinel using lithia as an additive (sampling designation BB1). No apparent residual lithia can be seen. However, when silica is added (Figure 10) films appear along grain edges. It is presumed that these films are silicious but as yet no quantitative study of the structure has been made.



*Figure 9. Typical Microstructure of Transparent Spinel BB1 Composition - 150X*

It is noted that the attainment of transparency can involve three recognized grain boundary migration control mechanisms, including deviation from stoichiometry, the addition of an impurity which acts to inhibit grain growth by solute hardening, and the introduction of inhibiting second phases. It will remain for future study to determine, with more confidence, which mechanism or combination of mechanisms are controlling.

TABLE I. SUMMARY OF SPINEL COMPOSITIONS STUDIED

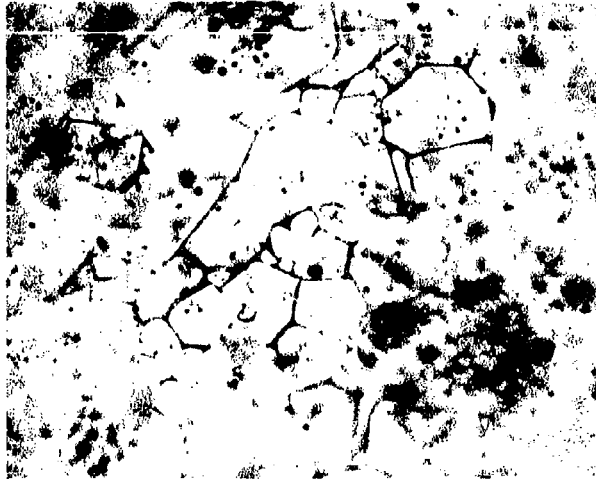
<u>Sample Designation</u>	<u>% Additives</u>	<u>Firing (g) Schedule</u>	<u>Pill Size</u>	<u>Remarks</u>
A (a)	none	Sequential	1/2 in. dia. 1/2 in. gm	White, low density
B	none			White, low density
C	none			White, low density
A <sub>p</sub> (b)	none			White, vitreous, dense, translucent
B <sub>p</sub>	none			White, vitreous, dense, translucent
C <sub>p</sub>	none			White, vitreous, dense, translucent
A <sub>ps</sub> (c)	2%			White, "puff ball" porosity with clean area around grain boundaries
B <sub>ps</sub>	2%			White, "puff ball" porosity with clean area around grain boundaries
C <sub>ps</sub>	2%			White, vitreous, dense, translucent large grain size (h)
A <sub>pl</sub> (d)	2%			Clean areas dispersed thru white areas, individual grains clear
B <sub>pl</sub>	2%			Clean areas dispersed thru white areas, individual grains clear
C <sub>pl</sub>	2%			White to grey, vitreous, dense, translucent, large grained
AA (e)	none		3/4 in. dia. 2 gm	White to grey, vitreous, dense, translucent, fine grained (i)
BB	none			"Sugar" appearance

TABLE I. SUMMARY OF SPINEL COMPOSITIONS STUDIED (Cont'd.)

Sample Designation	% Additives	Firing (g) Schedule	Pill Size	Remarks
CC	none	Sequential	3/4 in. dia. 2 gm	White to grey, vitreous, dense, translucent, large grained
AA <sub>s</sub>	2%			Transparent, small grain size, low transmission
BB <sub>s</sub>	2%			Transparent, small grain size, low transmission
CC <sub>s</sub>	2%			Translucent with large grain size (very dense)
AA <sub>l</sub>	2%			Transparent, small grain size, high transmission
BB <sub>l</sub>	2%			Transparent, small grain size, high transmission
CC <sub>l</sub>	2%			Translucent with large grain size (very dense)
AA <sub>sl</sub> (f)	2% each			Transparent, small grain size, high transmission
BB <sub>sl</sub>	2% each			Transparent, small grain size, high transmission
CC <sub>sl</sub>	2% each			Translucent with large grain size (very dense)
BB <sub>l</sub>	2%	1900°C 16 hrs.		White, high porosity – appears liquid lithia and SiC <sub>2</sub> boiling
BB <sub>s</sub>	2%	1900°C 16 hrs.		White, high porosity – appears liquid lithia and SiC <sub>2</sub> boiling

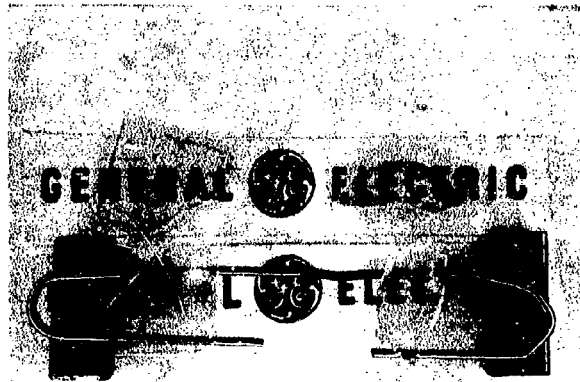
- (a) Single letter designates salt process – capital case designates composition  
 (b) Subscript p designates prepressed. All subsequent samples prepressed  
 (c), (d), (f) Subscript s designates silica additive, l lithia additive, and sl both additives  
 (e) Double capital case designates commercial powder process  
 (g) All but initial samples pre-fired 1 hour 1250°C in air  
 (h) "Large grain-size" averaged about .100 in. diameter  
 (i) "Small grain-size" averaged about .010 in. diameter

NOTE: Air and steam firings are not included in this summary. Also initial studies on constant temperature firings at 1700°C, 1800°C, 1900°C to 16 hours proved ineffective. Sequential sintering always increased density.



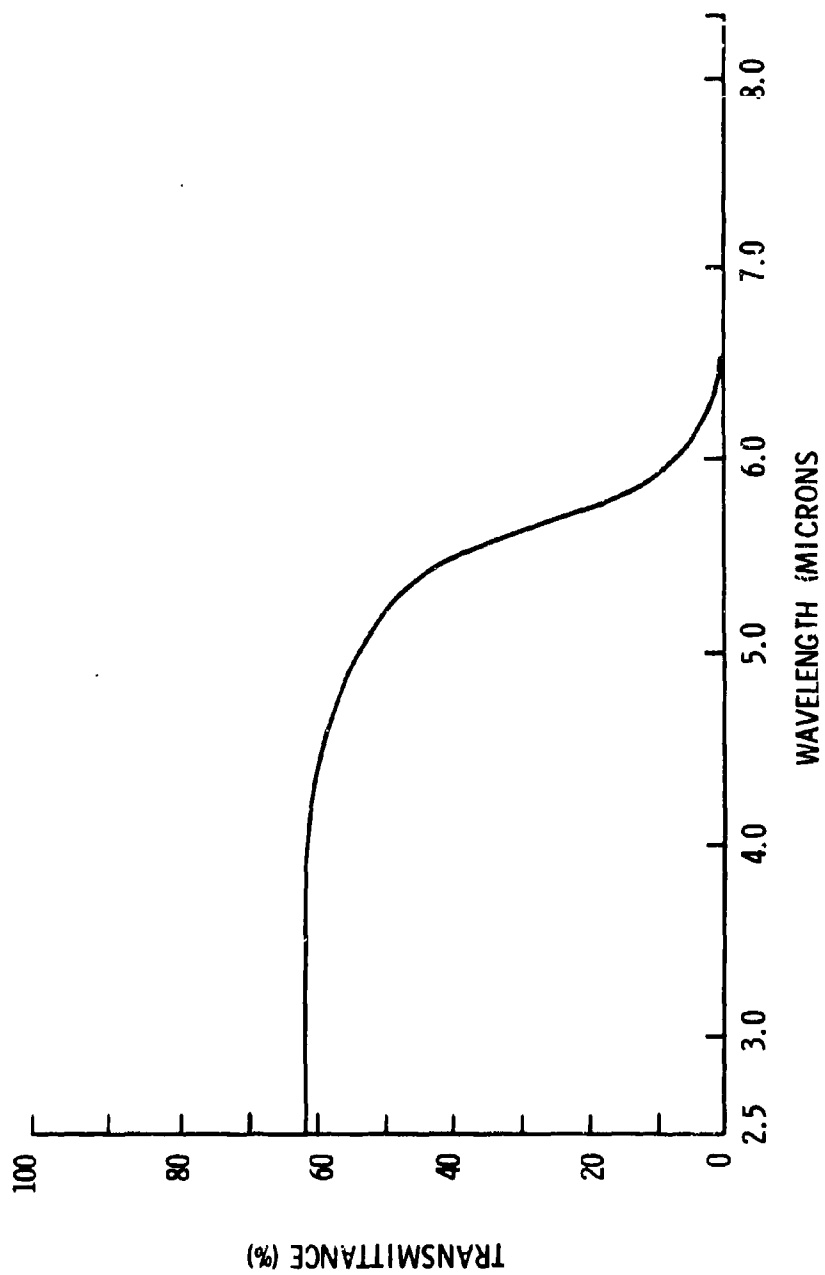
*Figure 10. Transmission Micrograph of Transparent Spinel BBsl-116X*

An example of the transparency of the material is shown in Figure 11. For comparison, a sample of Lucalox (samples on left photograph) is also included to demonstrate the effect of the birefringence of polycrystalline alumina and its inability to image, while the cubic isotropic spinel images without interference. Figure 12 is an infrared transmission curve for the material. Transmission behavior in the visible range is presently being determined.



*Figure 11. Photograph Demonstrating Transparency of Spinel (BBsl Composition) (on right) compared to Lucalox (on left)*





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Figure 12. Transmission Curve for Spinel in the Infrared (BBsl Composition)

## **V. CONCLUDING REMARKS**

Densities greater than 99% of theoretical are readily reached by most of the materials studied after sintering for one hour or longer at 1900°C in hydrogen. These specimens appear vitreous and are translucent or nearly transparent in thin sections.

Transparent specimens of compositions A and B containing 2% silica and lithia or both have been produced by sequential firing schedules which couple increasing temperature with decreasing times at temperature. All available processing techniques appear necessary including active sintering powders of uniform size and full density, high green density after pressing, sintering aids, prefiring and sequential final firing in hydrogen to 1900°C with adequate protection to prevent MgO vaporization.

## VI. FUTURE WORK

- (1) The mixing, drying, and calcining of magnesium and aluminum salts to produce high-purity, fine grained, theoretically dense spinel powders has been demonstrated. The process does involve the handling of large amounts of salts and liquids, however, and thus it is proposed that the more expeditious technique of mixing fine-grained individual constituents of alumina and magnesia be used.
- (2) Present studies have used compositions which straddled the 1900°C spinel phase field. Knowledge concerning grain growth inhibitions by solutes as exemplified by Lucalox<sup>®</sup>, Thoradox<sup>®</sup>, and Yttralox<sup>®</sup> points to specific quantities necessary to control grain-boundary migration rates. The effects of transparency of magnesia rich and alumina rich compositions will be studied since as the spinel compositions depart from the 50-50 area the solute effect increases in either direction.
- (3) Sintering aids, such as silica or lithia have thus far proved effective. These studies will be extended to determine the maximum and minimum quantities necessary and to try other additives with similar atomic characteristics.
- (4) It had been documented in earlier work by Bruch (3) that green densities greater than 35% were necessary before full density could be reached in Lucalox<sup>®</sup>. This result was also observed to be important in the Thoradox<sup>®</sup> and Yttralox<sup>®</sup> work. Present work on the spinel also confirms these observations. Thus precompaction techniques and possibly pressing lubricants will be studied to increase green densities.
- (5) Temperature and time at temperature are major processing parameters which must be controlled before the recently developed transparent spinel process can become reliable. The sequential firing (or step firing) schedules can also control grain-boundary migration rates and so prevent pore isolation and subsequent translucency rather than transparency. These schedules will be further documented and optimized.
- (6) Knowledge of the best composition in terms of grain size and clarity gained from (1) and (2) above will be used to determine which compositions are best suited for scale up and these materials will be optimized.
- (7) The process will be scaled up if feasible and will include studies concerning the effect of sample size, thickness, and shape on transparency.
- (8) Light transmission data will be accumulated.

- (9) Environmental effects which can affect clarity such as high humidity and salt spray will be studied.
  - (10) Cursory examination of the mechanical properties of spinel will be made as time permits and will include hardness, modulus, and strength determinations.
-

### ACKNOWLEDGEMENTS

The able assistance of Dr. M. J. Noone, Mr. V. Cordua, Mr. N. Grimm, and Mr. M. Birenbaum is gratefully acknowledged.

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13. ABSTRACT This final report covers the period from 15 September 1968 to 15 September 1969. The work was performed under Contract No. N00019-69-C-0133, Code AIR-5203A with Mr. C. Bersch of Naval Air Systems Command serving as Program Monitor.  A few transparent spinel samples have been made. Present studies involve the improvement of reproducibility and the characterization of the process and the material it produces. The results recorded thus far in the study are enumerated below:  <ol style="list-style-type: none"> <li>1) A process for producing high purity, fine grained, dense spinel powders has been demonstrated.</li> <li>2) A sintering furnace has been built which is cam controlled and is capable of maintaining temperatures of 1950°C for long times in hydrogen atmosphere. Other atmospheres can be introduced by using a molybdenum retort through which various gases, such as steam and wet hydrogen, can be piped.</li> <li>3) A few transparent specimens of both composition A and Composition B have been made.</li> <li>4) Thus far, additions of SiO<sub>2</sub> and LiO<sub>2</sub> are necessary to produce the transparent spinel materials.</li> <li>5) Densities greater than 99% of theoretical are readily reached by most of the materials after sintering for one hour or longer at 1900°C in hydrogen. These specimens appear vitreous and are translucent or nearly transparent in thin section (about 0.060 in. thick). Transparent specimens have been produced by sequential firing schedules which couple increasing temperatures with decreasing times at temperature. A typical 48 hour firing schedule would be 20 hours at 1600°C, 8 hours at 1700°C, 8 hours at 1800°C, and 8 hours at 1900°C in hydrogen atmosphere.</li> <li>6) Steam appeared to be a promising atmosphere for sintering spinels. Steam, rather than hydrogen, would have decided advantages in terms of cost and safety. However, firing schedules which produce transparent spinel in hydrogen atmosphere have not been duplicated in steam as yet.</li> </ol>			

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